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(54) Title: METAL SURFACE TREATMENT AGENT

(57) Abstract: The present invention relates to a metal surface treatment agent that characteristically contains (A) at least 1 vanadium compound and (B) at least one metal compound containing at least 1 metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium. The present invention also relates to a metal surface treatment method using the foregoing treatment agent and the corresponding surface-treated metals. The present invention provides a metal surface treatment agent that does not contain chromium and that can be used to impart an excellent corrosion resistance and alkali resistance to metals. The present invention provides a metal surface treatment method that uses the foregoing treatment agent and also provides the corresponding surface-treated metals.

## METAL SURFACE TREATMENT AGENT

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to a metal surface treatment agent and method that can be used to form a chromium-free coating on the surface of metal sheet coil and metal formed articles and that impart to such surfaces an excellent corrosion resistance and excellent alkali resistance. The invention also relates to the corresponding surface-treated metals.

More particularly, this invention relates to a metal surface treatment agent and method that can be used to form a chromium-free coating that imparts an excellent corrosion resistance and excellent alkali resistance to formed articles, castings, and sheet coil (for example, automotive body elements and other automotive parts, construction materials, parts for household electrical appliances) of zinciferous-plated steel sheet, steel sheet, or aluminiferous metal. The invention additionally relates to the corresponding surface-treated metals.

#### 2. Background Art

Metals such as zinciferous-plated steel sheet, steel sheet, and aluminiferous metals are susceptible to oxidation and corrosion by atmospheric

oxygen, moisture, and the ions present in moisture. One known method for inhibiting this corrosion comprises forming a chromate coating on the metal surface by bringing the metal into contact with a chromium-containing treatment bath, for example, a chromic acid chromate or phosphoric acid chromate bath.

5           While the coatings generated by these chromate treatments do tend to exhibit excellent corrosion resistance and excellent paint adherence, the treatment baths used in these treatments typically contain toxic hexavalent chromium, which can impose substantial time, labor, and cost burdens on wastewater treatment. Moreover, hexavalent chromium is also present in the coatings produced by these  
10           treatments, which has led based on environmental and safety considerations to an ever increasing tendency to avoid the use of these coatings.

Methods that employ non-chromate (chromium-free) treatments baths are known. For example, Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 7-278410 (278,410/1995) teaches a polymer composition and a method for treating metal surfaces wherein the polymer composition contains an acidic compound and a phenolic resin-type polymer with a specific structure. An agent and method for treating metal surfaces are also disclosed in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 8-73775 (73,775/1996). This agent and method provide an excellent fingerprint resistance.  
15           The agent contains at least 2 silane coupling agents having reactive functional groups with specific structures; these reactive functional groups are different from each other but are capable of reacting with one other. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 9-241576 (241,576/1997) discloses a method and agent for treating metal surfaces wherein the agent contains a silane  
20

coupling agent with a specific structure and a phenolic resin-type polymer with a specific structure. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 10-1789 (1,789/1998) teaches an agent and method for treating metal surfaces and metal surfaces thereby treated. This agent contains a specific 5 polyvalent anion and an organic polymer, such as an epoxy resin, acrylic resin, or urethane resin, that contains at least 1 nitrogen atom. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 10-60233 (60,233/1998) teaches a treatment method that uses two rust preventives (1) and (2) and metals thereby treated. Rust preventive (1) contains a bisphenol A epoxy resin with a specific 10 structure, while rust preventive (2) contains phenolic resin and a specific non-phenolic resin (e.g., polyester) in quantities that provide a solids ratio of 4: 1 to 1 : 4 upon mixing.

None of the metal surface treatments taught in these laid open patent applications uses chromium, and, while they do offer the advantage of a treatment 15 bath free of hexavalent chromium, in each case they produce coatings that exhibit a corrosion resistance inferior to the corrosion resistance from chromate treatment. The coatings produced by these chromium-free treatments also suffer from an unacceptable fingerprint resistance and lubricity.

Japanese Laid Open (Kokai or Unexamined) Patent Application 20 Number Hei 10-1789 teaches vanadic acid among the therein specified polyvalent anions. However, vanadic acid, which is an oxyacid of pentavalent vanadium, has a poor resistance to water and alkali. As a result, when the treated metal is rinsed, and particularly when it is rinsed with alkali, the vanadic acid is eluted from the coating, which results in a major reduction in corrosion resistance. This laid open patent

application also teaches the post-treatment execution of a water rinse and drying.

Thus, while the problem of a chromium-containing wastewater is not present, the organics create the problem of a COD-containing wastewater.

Inventions that use vanadium compounds as rust preventives are also known. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 1-9229 (9,229/1990) teaches an antirust paint that contains a film-forming resin, a phosphate ion source that releases phosphate ion in an ambient containing water and oxygen, and a vanadate ion source that releases vanadate ion in an ambient containing water and oxygen. Japanese Granted Patent 2,795,710 teaches an antirust composition in which specific compounds are blended in specific proportions; the specific compounds include (A) a vanadate ion source that releases vanadate ion in specific concentrations in a water-based dispersion and (B) an organophosphonic acid capable of dissolution in specific concentrations in a water-based dispersion. The vanadate ion source is added to function as the antirusting pigment of these antirust paints, and when baked at high temperatures (600°C and above) is converted to a pigment with an average particle size of several  $\mu\text{m}$ . The particles of this pigment do manifest an anticorrosion activity when present in paint films having a certain film thickness (several times the particle size of the pigment), but exhibit no anticorrosion activity at all in the thin films (no greater than several  $\mu\text{m}$ ) encountered in the field of metal treatment. Another problem with these treatment agents is that settling occurs due to aggregation of the particles therein when the treatment agent is allowed to stand.

Thus, no extant non-chromate metal surface treatment agent has the ability to form a coating that can simultaneously impart an excellent corrosion resistance, an excellent alkali resistance, and an excellent fingerprint resistance to metal surfaces.

5

## SUMMARY OF THE INVENTION

The present invention remedies the herein above described problems associated with the prior art. An object of the present invention is to provide a metal 10 surface treatment agent that does not contain chromium and that can impart an excellent corrosion resistance and excellent alkali resistance to metals. Additional objects of the present invention are to provide a metal surface treatment method that uses this agent and metals whose surface has been treated using the inventive agent and method.

15 The present inventors have discovered that highly corrosion-resistant, highly alkali-resistant coatings can be obtained by treating metal surfaces with a surface treatment agent whose essential components are a vanadium compound and a particular type of metal compound. This invention was achieved based on this discovery.

20 In specific terms, this invention relates to a metal surface treatment agent that characteristically contains: (A) at least 1 vanadium compound and (B) a metal compound or compounds containing at least 1 metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium.

In an embodiment preferred in order to obtain a better stability by the vanadium compound in the treatment agent and an improved corrosion resistance and alkali resistance by the produced film, the ratio in vanadium compound (A) of vanadium ion in the trivalent and tetravalent oxidation states to the total vanadium 5  $(V^{3+} + V^{4+})/V$  is in the range of 0.1 to 1.0.

In another preferred embodiment, the inventive metal surface treatment agent additionally contains (C) an organic compound that contains at least 1 functional group selected from the group consisting of hydroxyl groups, carbonyl groups, carboxyl groups, primary to tertiary amino groups, amide groups, phosphoric 10 acid groups, and phosphonic acid groups. The purpose of this embodiment is to reduce the pentavalent vanadium compound, when used, to the tetravalent or trivalent oxidation state and/or to improve the stability of the vanadium compound in 15 the inventive treatment bath.

In another embodiment preferred in order to improve the adherence of 15 the obtained coating, the inventive metal surface treatment agent additionally contains (D) at least 1 etchant selected from the group consisting of inorganic acids, organic acids, and fluorine compounds.

The invention additionally relates to a method for treating metal surfaces comprising treating a metal surface with any of the inventive metal surface 20 treatment agents described above, and drying by heating so the temperature of the metal reaches 50 to 250°C.

The invention further relates to surface-treated metals that bear a coating produced using the aforementioned inventive surface treatment method.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The vanadium compound present in the metal surface treatment agent  
5 of the present invention comprises at least 1 selection from vanadium compounds in  
which the vanadium has a pentavalent, tetravalent, or trivalent oxidation state.  
Examples of suitable vanadium compounds include, but are not necessarily limited  
to, pentavalent vanadium compounds such as vanadium pentoxide ( $V_2O_5$ ),  
metavanadic acid ( $HVO_3$ ), ammonium metavanadate, sodium metavanadate, and  
10 vanadium oxytrichloride ( $VOCl_3$ ), and trivalent and tetravalent vanadium  
compounds such as vanadium trioxide ( $V_2O_3$ ), vanadium dioxide ( $VO_2$ ), vanadium  
oxysulfate ( $VOSO_4$ ), vanadium oxyacetylacetone ( $VO(OC(CH_3)=CHCOCH_3)_2$ ),  
vanadium acetylacetone ( $V(OC(CH_3)=CHCOCH_3)_3$ ), vanadium trichloride  
15 ( $VCl_3$ ), and phosphovanadomolybdic acid { $H_{15-X}(PV_{12-X}Mo_xO_{40}) \cdot nH_2O$  ( $6 < x <$   
 $12$ ,  $n < 30$ )}.  
15

Preferably, the treatment agent of the present invention contains a  
trivalent or tetravalent vanadium compound as the vanadium compound (A). More  
preferably, the ratio of vanadium ions in the trivalent and tetravalent oxidation states  
to the total vanadium ( $V^{3+} + V^{4+})/V$  ( $V^{3+}$  refers to the mass of the vanadium in the  
20 trivalent oxidation state,  $V^{4+}$  refers to the mass of the vanadium in the tetravalent  
oxidation state, and  $V$  refers to the total mass of the vanadium) is in the range of 0.1

to 1.0, even more preferably in the range of 0.2 to 1.0, and most preferably in the range of 0.4 to 1.0. When this ratio is below 0.1, the stability of the vanadium in the treatment agent can be poor and the ultimately formed coating may have reduced corrosion resistance and alkali resistance.

5: Preferably, the ratio of vanadium ions in the pentavalent oxidation state ( $V^{5+}$ ) to the total vanadium is in the range of 0 to 0.9, even more preferably in the range of 0 to 0.8, and most preferably in the range of 0 to 0.6.

One process for introducing a trivalent or tetravalent vanadium compound into the treatment agent of the present invention comprises using at least one of the  
10 trivalent or tetravalent vanadium compounds described above. Another suitable process comprises effecting a preliminary reduction of a pentavalent vanadium compound to a trivalent or tetravalent vanadium compound using a reducing agent. The reducing agent used for this purpose may be inorganic or organic but preferably is organic. The use of the above-described compound (C) is particularly preferred.

15 The component (B) present in the inventive metal surface treatment agent of the present invention comprises a metal compound or compounds containing at least 1 metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium. Component (B) can preferably be an oxide or hydroxide of the specified metals, a complex of these metals, or the salt  
20 of an inorganic or organic acid. Suitable examples of metal compound (B) include, but are not necessarily limited to, zirconyl nitrate  $ZrO(NO_3)_2$ , zirconyl acetate, zirconyl sulfate, ammonium zirconyl carbonate  $(NH_4)_2(Zr(CO_3)_2(OH)_2)$ , dizirconium acetate, titanyl sulfate  $TiOSO_4$ , titanium lactate, diisopropoxytitanium

bisacetylacetone ( $C_5H_7O_2)_2Ti(OCH(CH_3)_2)_2$ , the reaction product of lactic acid and titanium alkoxide, molybdic acid  $H_2MoO_4$ , ammonium molybdate, sodium molybdate, molybdic acid compounds such as ammonium molybdophosphate  $(NH_4)_3(PO_4Mo_{12}O_{36})\cdot 3H_2O$  and sodium molybdophosphate

5       $Na_3(PO_4\cdot 12MoO_3)\cdot nH_2O$ , metatungstic acid  $H_6(H_2W_{12}O_{40})$ , ammonium metatungstate  $(NH_4)_6(H_2W_{12}O_{40})$ , sodium metatungstate, paratungstic acid  $H_{10}(W_{12}O_{46}H_{10})$ , ammonium paratungstate, sodium paratungstate, permanganic acid  $HMnO_4$ , potassium permanganate, sodium permanganate, manganese dihydrogen phosphate  $Mn(H_2PO_4)_2$ , manganese nitrate  $Mn(NO_3)_2$ , manganese sulfate, manganese fluoride, manganese carbonate  $MnCO_3$ , manganese acetate, 10      cerium acetate  $Ce(CH_3CO_2)_3$ , cerium nitrate, and cerium chloride.

The organic compound (C) present on an optional basis in the metal surface treatment agent of the present invention comprises an organic compound that contains at least 1 functional group selected from the group consisting of hydroxyl groups, carbonyl groups, carboxyl groups, primary to tertiary amino groups, amide groups, phosphoric acid groups, and phosphonic acid groups.

Suitable examples of organic compound (C) include, but are not necessarily limited to, alcohols such as methanol, ethanol, isopropanol, and ethylene glycol; carbonyl compounds such as formaldehyde, acetaldehyde, furfural, 20      acetylacetone, ethyl acetoacetate, dipivaloylmethane, and 3-methylpentanedione;

organic acids such as formic acid, acetic acid, propionic acid, tartaric acid, ascorbic acid, gluconic acid, citric acid, and malic acid; amine compounds such as triethylamine, triethanolamine, ethylenediamine, pyridine, imidazole, pyrrole, morpholine, and piperazine; acid amide compounds such as formamide, acetamide, 5 propionamide, and N-methylpropionamide; amino acids such as glycine, alanine, proline, and glutamic acid; organophosphoric acids such as aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1'-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), and phytic acid; monosaccharides such as glucose, mannose, and galactose; oligosaccharides such as maltose and 10 sucrose; natural polysaccharides such as starch and cellulose; aromatic compounds such as tannic acid, humic acid, ligninsulfonic acid, and polyphenols; and synthetic polymers such as polyvinyl alcohol, polyethylene glycol, polyacrylic acid, polyacrylamide, polyethyleneimine, and water-soluble nylon.

The use of the organic compound (C) is preferred for the purposes of 15 reducing pentavalent vanadium compound, when used, to the tetravalent or trivalent vanadium compound and/or improving the stability of the vanadium compound in the treatment bath of the present invention.

The organic compound (C) can be preliminarily mixed with the 20 vanadium compound with heating (for example, at 40 to 100°C for 5 to 120 minutes) to give a mixture in which the reduction and stabilization reactions have been thoroughly developed and the resulting mixture can then be blended into the surface treatment agent. Alternatively, the surface treatment agent in the form of a simple

mixture can be coated on the metal surface and reduction can be developed during the ensuing thermal drying step.

The etchant (D) present on an optional basis in the metal surface treatment agent of the present invention comprises at least 1 compound selected  
5 from inorganic acids, organic acids, and fluorine compounds.

The optional etchant (D) is used to etch the basis metal during application of the treatment agent or during the thermal drying step. Suitable examples of etchant (D) include, but are not necessarily limited to, inorganic acids such as phosphoric acid, nitric acid, and sulfuric acid; organic acids such as formic acid and acetic acid; and fluorine compounds such as hydrofluoric acid, fluoboric acid HBF<sub>4</sub>, fluosilicic acid H<sub>2</sub>SiF<sub>6</sub>, fluozirconic acid H<sub>2</sub>ZrF<sub>6</sub>, fluotitanic acid H<sub>2</sub>TiF<sub>6</sub>, stannous fluoride SnF<sub>2</sub>, stannic fluoride SnF<sub>4</sub>, ferrous fluoride, and ferric fluoride. Use of the etchant (D) is preferred for the purpose of improving the adherence of the ultimately obtained coating.  
10

The content of the constituent component in the treatment agent of the present invention is preferably as follows: for the vanadium compound (A), preferably 1 to 100 g/L as vanadium and more preferably 2 to 70 g/L as vanadium; for the metal compound (B), preferably 1 to 100 g/L as the metal and more preferably 2 to 70 g/L as the metal. The vanadium compound (A)/metal compound (B) mass ratio is preferably 1/9 to 9/1 calculated on the metal and is more preferably 2/8 to 8/2 calculated on the metal.  
15

The organic compound (C) is preferably added at from 0.05 to 10 mass parts and more preferably at from 0.1 to 5 mass parts, in each case per 1 mass

part pentavalent oxidation state vanadium in the vanadium compound. An addition in excess of that required for reduction is preferred in order to stabilize the reduced material in the treatment bath.

5. The etchant (D) is present preferably at 1 to 100 g/L and more preferably at 2 to 70 g/L.

The treatment agent of the present invention may also contain, to help improve the adherence and corrosion resistance of the coating, a metal sol such as a water-dispersible silica sol and/or alumina sol or zirconia sol; a silane coupling agent such as an aminosilane, epoxysilane, or mercaptosilane; and/or a water-soluble or 10 water-dispersible resin such as polyacrylic acid, polyacrylamide, or polyvinyl alcohol. When such a component is added, it is preferably added at from 5 to 40 mass% of the total nonvolatile component and more preferably at from 10 to 30 mass% of the total nonvolatile component.

For the purposes of this invention, the total nonvolatile component is 15 the component remaining after the surface treatment agent has been dried by heating for 2 hours at 110°C.

The solvent used in the surface treatment agent of the present invention preferably comprises mainly water, but may on an optional basis also contain a water-soluble organic solvent, e.g., an alcohol, ketone, or glycol ether, in 20 order to help improve the drying characteristics of the coating.

The surface treatment agent of the present invention may also contain, within a range that does not impair the essential features of the present

invention or the properties of the coating of the present invention, additives such as surfactant, defoamer, leveling agent, germicide/bactericide, and colorant.

The surface treatment method of the present invention will now be discussed.

5           The nature of the pretreatment for the surface treatment of the present invention is not particularly critical. As a general matter, surface treatment in accordance with the present invention will be preceded by cleaning with an alkaline or acidic degreaser, or hot water, or solvent, in order to remove any oils and contaminants present on the substrate. This can be followed on an optional basis by  
10          surface conditioning with acid or alkali. In a preferred embodiment, cleaning of the substrate surface is followed by rinsing with water so as to remove as much cleaning agent as possible from the substrate surface.

15          The treatment method of the present invention comprises application of the inventive surface treatment agent to the metal surface followed by drying by heating to 50 to 250°C; however, the techniques used for application and drying are not particularly critical.

20          The following application techniques will typically be used: roll coating, in which the treatment agent is applied to the substrate surface by transfer from a roll; broadcasting of the treatment agent over the substrate surface using, for example, a shower ring, followed by roll squeegee; dipping the substrate in a treatment bath; or spraying the treatment agent on the substrate. While the temperature of the treatment bath again is not specifically restricted, the treatment temperature is preferably from 0 to 60°C and is more preferably from 5 to 40°C

given that the solvent for the treatment agent of the present invention comprises mainly water.

The drying process does not necessarily require heating, and physical removal, for example, by air drying or air blowing, can be pursued. However, drying by the application of heat is preferred in order to improve the film-forming performance and increase the adherence. The temperature in such cases is preferably 5 50 to 250°C and more preferably 60 to 220°C.

Coating deposition is preferably from 0.005 to 1.5 µm as the dry film thickness and more preferably from 0.01 to 1.0 µm as the dry film thickness. 10 Acceptable corrosion resistance and overcoat adherence are not obtained at less than 0.005 µm, while deposition in excess of 1.5 µm runs the risk of producing cracks in the coating and a decline in adherence by the coating itself.

The formation of an organic polymer coating in a dry film thickness of 0.3 to 3.0 µm on the coating formed from the surface treatment agent of the 15 present invention, in addition to boosting the corrosion resistance and alkali resistance of the metal workpiece, can impart thereto fingerprint resistance, solvent resistance, and surface lubricity.

A preferred method for establishing this organic polymer coating comprises application of an overcoating agent (Z) whose main component is water- 20 soluble or water-dispersible organic polymer, followed by drying by heating at an attained substrate temperature of 50 to 250°C. The water-soluble or water-dispersible organic polymer used in the overcoating agent (Z) can be, for example, polymer as afforded by the polymerization of addition-polymerizable unsaturated

monomer, such as acrylic resins and polyolefin resins, as well as polymer as afforded by a condensation reaction, such as epoxy resins, urethane resins, polyester resins, polyamide resins, and phenolic resins. The glass-transition temperature of the subject organic polymer is preferably from 0 to 120°C and more preferably is from 5 10 to 100°C. A glass-transition temperature below 0°C may result in a coating with poor strength and hardness, while a glass-transition temperature in excess of 120°C may result in poor film-formability and poor adherence.

In addition to containing at least 1 selection from the foregoing organic polymers, the overcoating agent may preferably contain water-dispersible 10 silica in order to improve the toughness and fingerprint resistance of the coating. The addition of a water-borne wax may also be preferred in order to improve the lubricity. The preferred contents of the foregoing components are as follows: for the organic polymer, 50 to 100 mass parts nonvolatile component per 100 mass parts total nonvolatiles in the overcoating agent; for the water-dispersible silica, 0 to 40 15 mass parts nonvolatile component per 100 mass parts total nonvolatiles in the overcoating agent; and for the water-borne wax, 0 to 30 mass parts nonvolatile component per 100 mass parts total nonvolatiles in the ovecoating agent. A crosslinker capable of crosslinking the organic polymer may also be present.

In one embodiment of the invention, one or more water-soluble or water-dispersible organic polymers of the type described herein above may be incorporated 20 directly into the metal surface treatment agent as an additional component (E).

When coated on a metal substrate and dried thereon by heating, the surface treatment agent of the present invention reacts with the surface of the metal substrate and forms a fine, dense, and passive coating.

The manifestation of excellent corrosion resistance by the coating produced by the surface treatment agent of the present invention, without wishing to be bound to any particular theory, is believed to be due to a delocalization of the corrosion electrons (potential leveling) and a barrier effect by the coating that checks the permeation of oxygen, moisture, and ions. With respect to the vanadium compound (A) of the present invention, it is believed that a pentavalent vanadium compound occurs with the generation of an oxygen-bonded polyvalent anion and is unable to generate an entirely acceptable performance due to its poor water resistance and alkali resistance. However, a coating having improved water resistance and alkali resistance can be formed using a treatment agent of the present invention that contains reduced tetravalent and/or trivalent vanadium compounds.

The organic compound (C) is believed both to reduce the pentavalent vanadium compound and at the same time to chelate and stabilize the trivalent and/or tetravalent vanadium afforded by reduction in and present in the aqueous solution.

The use of an organic polymer-based overcoating on the inventive film can provide an additional and substantial boost in corrosion resistance due to a synergistic interaction with the barrier activity of the overcoating.

### Examples

The present invention is explained in greater detail hereinbelow by working and comparative examples. The working examples that follow are intended

only as individual examples and should not be construed as limiting the present invention. The procedures used to evaluate the treated sheet samples prepared in the working and comparative examples are also explained below.

5       **1. Substrates**

A : electrogalvanized steel sheet (sheet thickness = 0.8 mm)

B : hot-dip galvanized steel sheet (sheet thickness = 0.8 mm)

C : 55% Al/Zn-plated steel sheet (sheet thickness = 0.5 mm)

10      **2. Inventive treatment baths**

(1)     **Treatment bath components**

The vanadium compounds (A) used in the treatment baths were as follows.

A1 : ammonium metavanadate

15       A2 : vanadium pentoxide

A3 : vanadium trioxide

A4 : vanadium oxyacetylacetone

The metal compounds (B) used in the treatment baths were as follows.

20       B1 : ammonium molybdate

B2 : ammonium metatungstate

B3 : ammonium zirconium carbonate

B4 : fluotitanic acid

B5 : manganese carbonate

The organic compounds (C) used in the treatment baths were as follows.

C1 : L-ascorbic acid

5 C2 : D-glucose

C3 : glyoxal

The etchants (D) used in the treatment baths were as follows.

D1 : HF

D2 : H<sub>2</sub>ZrF<sub>6</sub>

10 D3 : CH<sub>3</sub>COOH

D4 : H<sub>2</sub>SiF<sub>6</sub>

(2) Preparation of the treatment baths

Examples 1 through 7: The vanadium compound (A), metal compound (B), etchant (D), and deionized water were mixed and heated at 50°C for 1 hour.

15 Examples 8 through 11: The vanadium compound (A) was first mixed into the 5% aqueous solution of the organic compound (C) followed by heating for 30 minutes at 80 to 100°C. After subsequently cooling to room temperature, the metal compound (B) and then the etchant (D) were added. The bath was finally brought to its prescribed concentration by the addition of deionized water.

### 3. Overcoating baths

The overcoating agents (Z) and treatment methods therewith are described below.

5 Z1: a water-borne treatment bath containing 10% nonvolatile fraction comprising 100 mass parts as solids of a water-borne polyurethane (SUPERFLEX 100 from Dai-ichi Kogyo Seiyaku Co., Ltd.), 20 mass parts as silica of a water-borne silica (SNOWTEX C from Nissan Chemical Industries, Ltd.), and 10 mass parts as solids of a water-borne wax (CHEMIPEARL W900 from Mitsui Chemicals, Inc.).

10 Z2: a water-borne treatment bath containing 20% nonvolatile fraction comprising 10 mass parts as silica of a water-dispersible silica and 100 mass parts as solids of an ammonia-neutralized water-borne polymer (ethylene-acrylic acid copolymer with ethylene/acrylic acid = 80/20 and average molecular weight = approximately 20,000).

15

### 4. Treatment sequence

#### (1) Degreasing

20 The substrate was degreased with an alkaline degreaser (PALKLIN 364S from Nihon Parkerizing Co., Ltd., 20 g/L bath, 60°C, 10-second spray, spray pressure = 50 kPa) and was then rinsed with water by spraying for 10 seconds.

#### (2) Coating with the treatment bath of the present invention and drying

I : the treatment bath was applied with a #3 bar coater followed by drying at a sheet temperature of 80°C using a convection oven.

5 II : the treatment bath was applied with a #3 bar coater followed by drying at a sheet temperature of 120°C using a convection oven.

(3) Coating with the overcoating treatment bath and drying

An overcoating bath as described above was bar-coated to a dry-film thickness of about 1 µm on the coating already formed using 10 the treatment bath and method of the present invention. This was followed by drying by heating at a sheet temperature of 100°C.

5. Evaluation procedures

15 (1) Corrosion resistance

The corrosion resistance was determined by salt-spray testing based on JIS Z-2371. After salt-spray exposure for 72 hours or 120 hours, the area of white rust production was scored on the following scale.

20 Evaluation scale:

area of white rust development

++ : less than 10%

+ : less than 30% but at least 10%

Δ : less than 60% but at least 30%

✗ : at least 60%

(2) Alkali resistance

A bath was prepared containing 20 g/L of the alkaline  
5 degreaser PALKLIN 364S from Nihon Parkerizing Co., Ltd. The resulting aqueous degreaser solution was adjusted to 60°C and then sprayed for 30 seconds on the already treated sheet. This was followed by rinsing with water and drying at 80°C. The sheet was subsequently evaluated for corrosion resistance using the conditions  
10 and methodology described in (1) above.

(3) Fingerprint resistance

A finger was pressed onto the surface of the treated sheet followed by evaluation by visual inspection of the status of the  
15 residual fingerprint trace.

Evaluation scale:

++ : residual fingerprint trace entirely absent

+ : very faint residual fingerprint trace

Δ : residual fingerprint trace present

20 ✗ : distinct residual fingerprint trace present

(4) Solvent resistance

An ethanol-soaked gauze was wrapped around a silicone rubber cube (1 cm) and this was rubbed back-and-forth 10 times on the test surface under 50,000 kPa.

Evaluation scale:

- 5            ++ : coating exfoliation almost entirely absent  
              + : slight exfoliation of the coating occurred  
              Δ : moderate exfoliation of the coating occurred  
              × : the coating was entirely exfoliated with exposure of the substrate

10

The treatment bath compositions and treatment methods used in the working and comparative examples are reported in Tables 1 and 2, while the evaluation results for the treated sheets are reported in Tables 3 and 4. The results reported in Table 3 confirm an excellent corrosion resistance and alkali resistance 15 for coatings produced from inventive treatment agents (Examples 1 through 11) containing the herein specified vanadium compound (A) and metal compound (B). In contrast, a poor corrosion resistance and poor alkali resistance were obtained in Comparative Examples 1 through 3, which either did not contain the vanadium compound (A) or did not contain the metal compound (B).

20

Examples 12 through 22 concerned the additional execution of a resin overcoating (Z1 or Z2) on the films produced in Examples 1 through 11. Examples 12 through 22 all gave an excellent corrosion resistance and alkali resistance as well as an excellent fingerprint resistance and solvent resistance. In contrast to this, a

poor corrosion resistance and poor alkali resistance were obtained in Comparative Examples 4 through 6, which either did not contain the vanadium compound (A) or did not contain the metal compound (B).

Table 1.

5

working and comparative examples	substrate	treatment bath composition in g/L				treatment method
		vanadium (A)*	(V <sup>3+</sup> + V <sup>4+</sup> ) /total V	metal compound (B)*	etchant (D)	
Example 1	A	A1 (7) A3 (18)	0.72	B1 (5) B4 (10)	—	I
Example 2	A	A1 (7) A3 (18)	0.72	B1 (5) B4 (10)	D2 (2)	I
Example 3	A	A4 (3)	1.0	B4 (2)	D2 (2)	I
Example 4	B	A2 (7.2) A3 (2.8)	0.28	B3 (10)	D1 (10)	II
Example 5	B	A1 (3) A3 (1) A4 (2)	0.5	B2 (2) B5 (5)	D2 (10)	II
Example 6	C	A3 (5) A4 (10)	1.0	B4 (10)	D4 (1)	I
Example 7	A	A1 (7)	0	B1 (5) B4 (10)	D1 (2)	I
Comparative Example 1	A	—	—	B1 (5) B4 (10)	D1 (2)	I
Comparative Example 2	B	A2 (7.2) A3 (2.8)	0.28	—	—	II

\* as the metal

Table 2.

working and comparative examples	substrate	treatment bath composition in g/L				treatment method
		vanadium (A)*	metal compound (B)*	organic compound (C)	etchant (D)	
Example 8	A	A1 (12)	B1 (5) B4 (5)	C1 (5)	D1 (2)	I
Example 9	B	A (7.5)	B2 (5)	C2 (7.5)	D3 (5)	II
Example 10	A	A1 (15)	B3 (15)	C3 (15)	D2 (5)	II
Example 11	C	A1 (10) A2 (20)	B4 (6) B5 (4)	C1 (1)	D4 (10)	I
Comparative Example 3	A	A1 (12)	—	C1 (5)	D1 (2)	I

\* as the metal

5                   Example 12: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 1.

Example 13: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 2.

10                  Example 14: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 3.

Example 15: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Example 4.

Example 16: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 5.

15                  Example 17: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Example 6.

Example 18: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 7.

Example 19: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Example 8.

5 Example 20: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Example 9.

Example 21: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Example 10.

10 Example 22: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Example 11.

Comparative Example 4: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Comparative Example 1.

Comparative Example 5: Treatment with overcoating agent Z1 was carried out on film formed in accordance with Comparative Example 2.

15 Comparative Example 6: Treatment with overcoating agent Z2 was carried out on film formed in accordance with Comparative Example 3.

Table 3.

working and comparative examples	corrosion resistance after SST for 48 hours	alkali resistance after SST for 48 hours
Example 1	+	+
Example 2	++	++
Example 3	+	+
Example 4	++	+
Example 5	++	++
Example 6	++	++
Example 7	+	Δ
Example 8	++	++
Example 9	++	++
Example 10	++	++
Example 11	++	++
Comparative Example 1	Δ	×
Comparative Example 2	Δ	×
Comparative Example 3	Δ	×

Table 4.

working and comparative examples	corrosion resistance after SST for 120 hours	alkali resistance after SST for 120 hours	fingerprint resistance	solvent resistance
Example 12	+/++	+/++	+	+
Example 13	++	++	++	++
Example 14	++	+	+	++
Example 15	++	++	++	++
Example 16	++	++	++	++
Example 17	++	++	++	++
Example 18	+	+/ $\Delta$	++	++
Example 19	++	++	++	++
Example 20	++	++	++	++
Example 21	++	++	++	++
Example 22	++	++	++	++
Comparative Example 4	$\Delta$	$\times$	+	$\Delta$
Comparative Example 5	$\Delta$	$\times$	+	$\Delta$
Comparative Example 6	$\Delta$	$\times$	+	$\Delta$

The treatment agent of the present invention is a non-chromate treatment agent that is free of toxic chromium compounds. The film or coating formed from the inventive surface treatment agent exhibits a corrosion resistance that is as good as or better than the corrosion resistance of prior-art chromate coatings. As a consequence of these features, the inventive surface treatment agent,

surface treatment method, and surface-treated metals will have a very high commercial and industrial utilization value.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.

Moreover, the terms "a" and "an", as used herein, mean one or more unless clearly indicated to the contrary, and the term "as the metal" means calculated based on the amount of the metal in a compound.

**WHAT IS CLAIMED:**

1. A metal surface treatment agent comprising:
  - (A) at least 1 vanadium compound; and
  - (B) at least one metal compound containing at least 1 metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium.
2. The metal surface treatment agent of claim 1, wherein the ratio in the vanadium compound (A) of vanadium ions in the pentavalent oxidation state to the total vanadium  $V^{5+}/V$  is in the range of 0 to 0.6.
3. The metal surface treatment agent of claim 1 or 2, further comprising (C) an organic compound that contains at least 1 functional group selected from the group consisting of hydroxyl groups, carbonyl groups, carboxyl groups, primary to tertiary amino groups, amide groups, phosphoric acid groups, and phosphonic acid groups, wherein the organic compound (C) is present in an amount of 0.05 to 10 mass parts per 1 mass part pentavalent oxidation state vanadium in the vanadium compound.
4. The metal surface treatment agent of any of claims 1 to 3, further comprising (D) at least 1 etchant selected from the group consisting of inorganic acids, organic acids, and fluorine compounds, wherein the etchant (D) is present in an amount of 1 to 100 g/l.

5

5. The metal surface treatment agent of any of claims 1 to 4, wherein the vanadium compound (A) is present in an amount of 1 to 100 g/l as vanadium and the metal compound (B) is present in an amount of 1 to 100 g/l as metal.

10

6. The metal surface treatment agent of any of claims 1 to 5, wherein the vanadium compound (A)/metal compound (B) mass ratio is 1/9 to 9/1 calculated on the metal.

15

7. The metal surface treatment agent of any claims 1-6, further comprising (E) a water-dispersible or water-soluble organic polymer.

8. A method for treating a metal surface comprising:  
treating the metal surface with a metal surface treatment agent according to any of claims 1 to 7; and  
drying by heating so the temperature of the metal reaches 50 to 250°C.

20

9. A surface-treated metal that bears a coating formed using the surface treatment method of claim 8.

10. A surface-treated metal that bears a coating formed using the surface treatment agent of any of claims 1 to 7.

5

11. A surface-treated metal of claim 10 further comprising an organic polymer coating, wherein the organic polymer coating comprises a water-dispersible or water-soluble organic polymer having a glass transition temperature of 0 to 120°C.

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**WO 01/086016 A3**

(54) Title: METAL SURFACE TREATMENT AGENT

(57) Abstract: The present invention relates to a metal surface treatment agent that characteristically contains (A) at least 1 vanadium compound and (B) at least one metal compound containing at least 1 metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium. The present invention also relates to a metal surface treatment method using the foregoing treatment agent and the corresponding surface-treated metals. The present invention provides a metal surface treatment agent that does not contain chromium and that can be used to impart an excellent corrosion resistance and alkali resistance to metals. The present invention provides a metal surface treatment method that uses the foregoing treatment agent and also provides the corresponding surface-treated metals.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/15468

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C23C 22/05, 22/40  
 US CL : 148/247, 248, 251, 252, 275; 106/14.21, 14.44

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 148/247, 248, 251, 252, 275; 106/14.21, 14.44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 Please See Continuation Sheet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,264,378 A (OPPEN et al.) 28 April 1981, abstract, examples and claims.	1-2
X	US 4,298,404 A (GREENE) 03 November 1981, abstract, examples and claims.	1-3
X	US 4,992,115 A (IKEDA) 12 February 1991, abstract, examples and claims.	1-2
X	US 5,550,006 A (LARSON et al.) 27 August 1996, abstract, examples and claims.	1-2
X	US 6,027,579 A (DAS et al.) 22 February 2000, abstract, examples and claims.	1-2
X	WO 99/29927 A2 (HENKEL CORPORATION) 17 June 1999, abstract, examples and claims.	1-3
X	WO 00/24948 A1 (HENKEL CORPORATION) 04 May 2000, abstract, examples and claims.	1-2
X	JP 4-128384 A (NIPPON PAINT CO LTD) 28 April 1992, abstract.	1-2

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/15468

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claim Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claim Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claim Nos.: 4-11  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

  

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.